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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the thermally conductive resin sheet which was excellent in thermal conductivity, pliability, and shape flattery nature especially about the thermally conductive resin sheet used for uses, such as heat dissipation.

[0002]

[Description of the Prior Art]The constituent which makes it come as a thermally-conductive-resin constituent which has pliability to fill [a filler with high thermal conductivity] up the material which used silicone rubber and silicone oil as the base is known. Such a constituent intervenes between heating elements, such as an electric electronic component, and a radiation fin, and is used the making generation of heat from an electric electronic component radiate purpose, for example.

[0003]However, although it was flexible, and shape flattery nature is high and it might fully be stuck to it by electronic parts when the above-mentioned thermally-conductive-resin constituent was made to intervene between electronic parts and a radiation fin, since intensity was weak, there was a possibility of damaging at the time of handling.

[0004]In order to solve the above problems, the thermally conductive resin sheet which adds glass fiber, glass fabrics, etc. as a reinforcing member to a thermally-conductive-resin constituent is proposed (JP,7-14950,A etc.). However, there was a problem that a manufacturing process became complicated and cost became high, by using a reinforcing member.

[0005]In order to have improved thermal conductivity in the conventional thermally-conductive-resin constituent, had to raise the content of the thermally conductive filler, but. The adhesion of a thermally-conductive-resin constituent and a heating element fell, and there was a fault that a thermally-conductive-resin constituent Plastic solid exfoliated easily from a heating

element as the content of the thermally conductive filler became high.

[0006]Although thermal conductivity was raised in a thermally conductive material which used conventional silicone rubber as the base as the fill ration of the thermally conductive filler was raised, it was difficult for pliability to fall and to reconcile high thermal conductivity and good pliability.

[0007]

[Problem(s) to be Solved by the Invention]The purpose of this invention is it not only to to excel in thermal conductivity, but to provide a good thermally conductive resin sheet in the adhesion over pliability, a mechanical strength, and the portion applied in view of the actual condition of the conventional technology mentioned above.

[0008]

[Means for Solving the Problem]A thermally conductive resin sheet concerning this invention consists of foam in a range whose expansion ratio is 1.1 to 5.0 including elasticity resin and a thermally conductive filler.

[0009]Acrylic resin which is excellent in adhesion over an application site, and can improve pliability preferably as the above-mentioned elasticity resin is used. The above-mentioned thermally conductive filler is filled up with a specific aspect of affairs of this invention so that 5 - 90 volume % may be occupied.

[0010]Hereafter, details of this invention are explained. The above-mentioned elasticity resin is used in order to improve adhesion and pliability over an application site. As elasticity resin, especially as long as good pliability and adhesion over an application site may be revealed, it is not limited, but thermoplastics or thermosetting resin can be used. Preferably An acrylic resin; ethylene-vinylacetate copolymer, an ethylene methyl methacrylate copolymer (EMMA), Elasticity olefin system resin, such as metallocene polyethylene; A styrene isoprene styrene copolymer (SIS), Styrene Butadiene Styrene (SBS), a styrene ethylene-butylene-styrene copolymer (SEBS), Elasticity styrene resin, such as a styrene ethylene-propylene-styrene copolymer (SEPS); cross linked rubber; denaturation silicone resin, such as thermoplastic-elastomer; silicone rubber, such as urethane elastomer, an ester elastomer, and an amide elastomer, etc. are mentioned.

[0011]Especially as the above-mentioned elasticity resin, acrylic resin is preferred. When acrylic resin is used, pliability and adhesion over an application site can be improved further. What was obtained by polymerizing acrylic acid acrylic ester which has an alkyl group of the carbon numbers 1-14 (meta) as acrylic resin is used.

[0012]As the above-mentioned (meta) acrylic ester, for example Methyl acrylate (meta), Ethyl acrylate, acrylic acid (meta) n-propyl, acrylic acid (meta) isopropyl, (Meta) Acrylic acid n-butyl, acrylic acid (meta) sec-butyl, (Meta) Acrylic acid t-butyl, cyclohexyl methacrylate, acrylic acid (meta) n-octyl, acrylic acid isooctyl, 2-ethylhexyl acrylate (meta), acrylic acid isononyl, acrylic

acid (meta) lauryl, etc. can be mentioned.

[0013]In this specification, an acrylic (meta) names an acrylic and methacrylic one generically. Only one sort may be used and two or more sorts of above-mentioned (meta) acrylic ester may be used together.

[0014]In order that the above-mentioned acrylic resin may adjust glass transition temperature of resin and polarity which are obtained, copolymerization of other vinyl monomers may be carried out. As such a copolymerizable vinyl monomer, For example, a styrene monomer represented by alpha-methylstyrene, vinyltoluene, styrene, etc.; The methyl vinyl ether, A vinyl ether system monomer represented by ethyl vinyl ether and isobutylvinyl ether; Fumaric acid, Monoalkyl ester of fumaric acid, dialkyl ester of fumaric acid, Monoalkyl ester of maleic acid and maleic acid, dialkyl ester of maleic acid, Unsaturated carboxylic acid or unsaturated carboxylic acid alkyl ester, such as monoalkyl ester of itaconic acid and itaconic acid; (meta) Acrylic nitril, Butadiene, isoprene, VCM/PVC, a vinylidene chloride, vinyl acetate, vinyl ketone, vinyl pyrrolidone, vinylpyridine, acrylamide (meta), vinylcarbazole, etc. can be mentioned.

[0015]As for the above-mentioned acrylic resin, it is desirable to contract an end by an unsaturated double bond of radical polymerization nature as a copolymerization ingredient, and to be in the range of the number average molecular weights 800-30000 preferably, and to carry out the graft copolymerization of polymer (X) whose glass transition temperature is not less than 30 **. Since a segment of high glass transition temperature by which copolymerization was carried out forms a frozen phase and reveals a false bridge construction operation by such graft copolymerization, acrylic resin with strong cohesive force can be obtained. Therefore, a thermoplastic resin sheet which was excellent in intensity using this acrylic resin can be obtained. Acrylic resin produced by doing in this way is a hot melt type, and its frozen phase is thermally reversible and it is fused above glass transition temperature. Therefore, melt kneading with a thermally conductive filler and sheet size enlargement by extrusion molding can be performed easily.

[0016]It is not limited, especially as long as other polymerization nature monomers, a copolymerizable double bond, and a number average molecular weight are 800-30000 as the above-mentioned polymer (X) and glass transition temperature is not less than 30 **. Other polymerization nature monomers and a copolymerizable double bond mean an unsaturated double bond of radical polymerization nature, and a vinyl group, an acrylyl group (meta), an allyl group, etc. can be mentioned as a functional group which has such an unsaturated double bond.

[0017]Since cohesive force as a polymer is hard to be obtained, and it becomes difficult to polymerize in being larger than 30000 when a number average molecular weight of the above-mentioned polymer (X) is smaller than 800, it is not desirable.

[0018]When glass transition temperature of the above-mentioned polymer (X) is smaller than

30 **, since ordinary temperature of condensation of a frozen phase is insufficient, it is not [that cohesive force as a polymer is hard to be obtained] desirable. Toagosei chemicals company make and trade name:AA-6 can be mentioned as a concrete example of the above-mentioned polymer (X).

[0019]A rate in acrylic resin of the above-mentioned polymer (X) has five to 100 preferred weight section to acrylic ester 100 weight section, and is more preferred. [of ten to 30 weight section] When there are few rates of polymer (X) than five weight sections, cohesive force as a polymer is hard to be obtained, and when more than 100 weight sections, practicality falls that gelling is imitated and it is easy to come.

[0020]A bridge may be constructed over the above-mentioned acrylic resin in order to heighten cohesive force. Especially about a crosslinking method, it is not limited but arbitrary methods, such as chemicals bridge construction or optical bridge construction, can be used. A method, for example, using an isocyanate cross-linking agent, an aziridine system cross linking agent, an epoxy cross-linking agent, etc. as chemicals bridge construction is mentioned. As optical bridge construction, a crosslinking method by radiation-induced crosslinking and UV irradiation, such as an electron beam, is mentioned, for example.

[0021]Acrylic resin and a thermally conductive filler may be kneaded and mixed in the state of no constructing a bridge, After carrying out size enlargement of the resin composition produced by it by being able to blend more thermally conductive fillers and doing in this way to a sheet shaped, by back-constructing a bridge, a thermally conductive resin sheet excellent in thermal conductivity and intensity can be obtained, and it is desirable.

[0022]To the above-mentioned acrylic resin, tackifiers, such as petroleum resin, hydrogenation petroleum resin, coumarone-indene resin, and rosin system resin, may be added. By addition of a tackifier, a thermally conductive resin sheet which was further excellent in adhesion over an application site can be obtained.

[0023]Although the above-mentioned acrylic resin can be obtained by arbitrary methods, such as solution polymerization and mass polymerization, it can dissolve the above-mentioned (meta) acrylic acid alkyl ester, for example in suitable solvents, such as ethyl acetate, and can usually be easily obtained by a solution polymerization method using a polymerization initiator. A method of polymerizing by irradiating with ultraviolet rays into an inert atmosphere of nitrogen etc. may be used to a non-solvent liquid mixture containing the above-mentioned (meta) acrylic acid alkyl ester and a photopolymerization initiator.

[0024]It is not limited especially as a molecular weight of the above-mentioned elasticity resin, for example, a thing of the range of 10,000-4 million is suitably used with weight average molecular weight. When weight average molecular weight is smaller than 10,000, intensity and elongation of a thermally conductive resin sheet may fall, when larger than 4 million, it becomes difficult to carry out kneading with a thermally conductive filler, and intensity of a

thermally conductive resin sheet may fall.

[0025]Glass transition temperature of elasticity resin has the preferred range of -120°C to $+20^{\circ}\text{C}$, and -100°C - especially 0°C are preferred. When glass transition temperature is lower than -120°C , it is hard to carry out composition of thermoplastics, and when higher than 20°C , the pliability of a thermally conductive resin sheet may fall.

[0026]Although viscosity in particular of elasticity resin is not restricted, the range of 100 cps - 100,000 cps (25°C) is preferred. When viscosity is less than 100 cps, are filled up with a thermally conductive filler, and kneading and when making it mix, shearing force is not transmitted easily. If thermally conductive filler particles condense, or it does not distribute uniformly in elasticity resin, but it becomes difficult to be mixed and it exceeds 100,000 cps, it will become difficult to distribute a thermally conductive filler, and will become difficult to be mixed as viscosity becomes high too much and increases a fill ration.

[0027]Especially as the above-mentioned thermally conductive filler, it is not limited but a publicly known filler blended into a thermally-conductive-resin constituent can usually be used suitably. As an example of such a thermally conductive filler, alumina, magnesium oxide, Oxides, such as beryllium oxide, titanium oxide, and a zinc oxide, boron nitride, Inorganic fillers, such as nitriding aluminum, silicon nitride, and silicon carbide, copper, silver, iron, Metal alloy fillers, such as metal fillers, such as aluminum and nickel, and titanium, What silica powder, such as carbon system fillers, such as a diamond, carbon fiber, and carbon black, quartz, and silica glass, was used, and carried out surface coating of silver, copper, etc. and the carbon material to inorganic filler particles, and a thing which carried out surface coating of an inorganic material or the carbon material to metal filler particles may be used. These may be used independently and may be used together two or more kinds.

[0028]As the above-mentioned thermally conductive filler, in order to raise compatibility with resin used as these fillers and bases, a filler which performed various surface treatments, such as silanizing, may be used. It is not limited in particular for particle shape, and a globular shape, a needle, fibrous, the shape of a scale, the shape of resin, plate-like, an infinite form, etc. are used.

[0029]Loadings of the above-mentioned thermally conductive filler have good 5 - 90 volume %, and are usually 20 to 80 volume % preferably. If thermal conductivity is not sometimes enough when content of a thermally conductive filler is less than 5 volume %, and 90 volume % is exceeded, hardness of a constituent will become high, adhesion flattery nature to unevenness of the surface of a radiating member is bad, thermal contact resistance increases, and efficient thermal conductivity may not no longer be obtained.

[0030]Various additive agents, such as a physical-properties regulator, a plasticizer, colorant, and fire retardant, may be added to the above-mentioned thermally-conductive-resin constituent which constitutes a thermally conductive resin sheet concerning this invention if

needed.

[0031]As the above-mentioned physical-properties regulator, as various silane coupling agents. For example, vinyltrimethoxysilane, dimethyldimethoxysilane, Methyl trimethoxysilane, methyl triethoxysilane, a tetramethoxy silane, A tetraethoxysilane, phenyltrimethoxysilane, diphenyldimethoxysilane, 3-aminopropyl trimethoxysilane, 3-aminopropyl methyl dimethoxysilane, 3-aminopropyl triethoxysilane, N-(2-aminoethyl)-3-aminopropyl triethoxysilane, N,N'-bis- [3-(trimethoxysilyl) propyl] Ethylenediamine, N,N'-bis- [3-(triethoxy silyl) propyl] Ethylenediamine, N,N'-bis- [3-(trimethoxysilyl) propyl] Hexaethylenediamine, N,N'-bis- [3-(triethoxy silyl) propyl] Hexaethylenediamine etc. are mentioned, and these are independent, or can use together and use two or more sorts.

[0032]It is preferred to blend a plasticizer with a resin composition of this invention further, in order to maintain pliability. As the above-mentioned plasticizer, for example Phosphoric ester, such as tributyl phosphate and tricresyl phosphate. Fatty acid monobasic acid ester species, such as phthalic ester, such as dioctyl phthalate, and glycerin monooleyl acid ester, Process oil, such as polyether, such as fatty acid dibasic acid esters, such as dioctyl adipate, propylene glycols, and ethylene glycol, and liquid hydrocarbon, etc. are mentioned, and these are independent, or can use together and use two or more sorts.

[0033]A dripping inhibitor, an antioxidant, an antiaging agent, an ultraviolet ray absorbent, a solvent, perfume, paints, a color, etc. may be further added by resin composition of this invention if needed. It faces manufacturing the above-mentioned resin composition for obtaining a thermally conductive resin sheet concerning this invention, and elasticity resin, a thermally conductive filler, and if needed, other ingredients are added and a method of kneading and mixing is used. As kneading and a mixing method, it is in a state which fused ** elasticity resin, and a thermally conductive filler is added and a method of kneading and mixing, a method of adding a thermally conductive filler and carrying out desolventization after kneading and mixing, where ** elasticity resin is diluted with a suitable solvent, etc. are mentioned, for example. ** Since the method can knead and mix a lot of thermally conductive fillers uniformly efficiently, it is suitable for obtaining a thermally conductive resin sheet of high thermal conductivity.

[0034]Especially as a device used for above-mentioned kneading and mixing, it is not limited and common devices, such as a kneading machine, an extrusion machine, a mixer, a roll, a kneader, and an agitator, can be used, for example. Necessity may be accepted, and inside of a device may be decompressed and deaerated at the time of kneading and mixing.

[0035]A thermally conductive resin sheet concerning this invention is obtained by making the above-mentioned resin composition foam with low magnification, and fabricating it to a sheet shaped. Although not limited in particular for the above-mentioned foaming method, for example, a foaming agent is added to the ** above-mentioned resin composition, a foaming

agent is added to the bridge construction foaming method and ** resin composition which are made to construct a bridge and foam under existence of a cross linking agent and a bridge construction auxiliary agent, and the unconstructed bridge foaming method etc. which are made to foam without constructing a bridge are mentioned.

[0036]As the above-mentioned foaming agent, as an organic blowing agent, for example Azo compounds, such as azocarbonyl amide and azobisisobutyronitrile, Sulfonylhydrazide compounds, such as nitroso compounds, such as N,N'-dinitroso pentamethylene tetramine, p-tosyl hydrazide, and a p,p'-oxybis(sulfonylhydrazide) (benzenesulphonyl hydrazide), etc. are used. A microcapsule which included volatile hydrocarbon compounds, such as chlorofluorocarbon, carbon dioxide and water, and pentane, and these gas system foaming agents is used as a foaming agent of a gas system, for example. As such a microcapsule, Expancel by a Japanese ferrite company is mentioned, for example.

[0037]As a method of making it foam, a method of generating foaming gas, a method of generating foaming gas by opening a pressure from a pressurization state, etc. are employable by heating or reacting a foaming agent.

[0038]As the bridge construction technique in bridge construction foaming, a method of using an electron beam, and a chemical formula method using a cross linking agent are mentioned, for example. As the above-mentioned cross linking agent, a polyfunctional organic compound which has reactant groups, such as water cross linking agent; epoxy, such as polyfunctional isocyanates, such as silane compounds, such as organic peroxide; BICHRU triethoxysilane, such as dicumyl peroxide, and MDI, and oxazoline, is used, for example. As the above-mentioned bridge construction auxiliary agent, condensation catalysts, such as polyfunctional monomer, such as divinylbenzene, and a dibutyltin JIRAURI rate, are used, for example.

[0039]In order that expansion ratio in a resin sheet of this invention may reconcile high heat conductivity and pliability, it is 5.0 from 1.1 times and its 3.0 times are preferred from 1.5 times. When expansion ratio becomes smaller than 1.1 times, pliability may be insufficient, and when it becomes larger than 5.0 times, thermal conductivity may fall.

[0040]It is not limited in particular for a forming process of a thermally conductive resin sheet concerning this invention, but various methods, such as sheet-izing by extrusion molding, calender molding, press forming, cast molding, and coating, sheet-izing by a belting press, and cutting, can be used. Foaming and size enlargement may be performed simultaneously, post expansion which carried out size enlargement to a sheet shaped may be performed, and size enlargement may be carried out to a sheet shaped after foaming.

[0041]As mentioned above, by making a thermally-conductive-resin constituent foam with low magnification, thermal conductivity is high and a thermally conductive resin sheet which was further excellent in pliability and adhesion over an application site is obtained.

[0042]

[Embodiment of the Invention]Although by describing a concrete example explains this invention to details more hereafter, this invention is not limited to the following examples.

[0043](Used material)

An elasticity resin-acrylic resin agitator, a cooler, a thermometer, and a nitrogen gas feed port to the separable flask of 2L which it had ** Acrylic acid butylester (BA)450g, The end is contracted by the unsaturated double bond of radical polymerization nature, and number average molecular weights are 800-30000, Glass transition temperature blended 451 g of toluene with the Toagosei make, poly-methyl-methacrylate macromere, and trade name:AA-6 (glass-transition-temperature [of 110 **], number average molecular weight 6000)90g as polymer (X) which is not less than 30 **. Temperature up of the monomer mixed solution was carried out using the water bath, nitrogen gas having replaced the inside of a separable flask, and agitating on 100-rpm conditions, after removing dissolved oxygen by carrying out bubbling of the above-mentioned monomer solution for 20 minutes using nitrogen gas.

[0044]When reflux was checked by the condenser tube, the solution which dissolved 0.3 g of 1,2-Jl (t-hexyl peroxy)-3,3,5-trimethylcyclohexane (the NIPPON SHOKUBAI [Co., Ltd.] make, a trade name: par hexa TMH) in about 1-g ethyl acetate was thrown in as a polymerization initiator, and the boiling point polymerization was started.

[0045]1 hour after starting the polymerization, the solution which dissolved par hexa TMH0.6g in about 1-g ethyl acetate was thrown in again. After starting the polymerization, the solution which dissolved the Jl (3,5,5-trimethylhexanoyl) peroxide (the Nippon Oil & Fats [Co., Ltd.] make, a trade name: par roil 335) 0.6g, 1.2g, and 1.8g in about 1-g ethyl acetate was thrown in 2 hours, 3 hours, and 4 hours afterward, respectively. Acrylic resin was obtained by performing the boiling point polymerization of 8 hours.

[0046]** Thermally conductive filler -- The DENKI KAGAKU KOGYO K.K. make, boron nitride SGP [0047]** Foaming agent -- Japan ferrite company make, isobutane intension vinylidene chloride acrylonitrile copolymer hollow particles, a trade name : Expancel DU120 [0048] (Examples 1 and 2) The above-mentioned acrylic resin, the thermally conductive filler, and the foaming agent were agitated until it was uniformly mixed using the defoaming agitator, and the thermally-conductive-resin constituent was prepared so that it might become the quantity shown in the following table 1. Thus, it slushed into the mold, and at 120 **, it was neglected for 2 hours or more, the obtained thermally-conductive-resin constituent was foamed and stiffened, and the thermally conductive resin sheet 1.5 times the expansion ratio of this was obtained.

[0049](Comparative example 1) silicone rubber (the Shin-Etsu Chemical Co., Ltd. make.) of the specified quantity shown in the following table 1 Trade name: KE12, the silicone rubber hardening agent (the Shin-etsu chemicals company make, lot number:CAT-RM), and the thermally conductive filler (the DENKI KAGAKU KOGYO K.K. make, boron nitride SGP) were

agitated until it was uniformly mixed using the defoaming agitator, and the thermally-conductive-resin constituent was prepared. This resin composition was slushed into the mold, and at the room temperature, it was neglected for 40 hours or more, and hardened, and the thermally conductive resin sheet was obtained.

[0050](Evaluation of an example and a comparative example) ** thermal conductivity, ** surface hardness, ** tensile strength, and ** initial adhesion were evaluated by the following ways about the thermally conductive resin sheet obtained by the above-mentioned Examples 1 and 2 and a comparative example.

[0051]** Thermal conductivity was measured by thermal conductivity Kyoto Electronics Manufacturing Co., Ltd. make and lot number:QTM-D3.

[0052]** According to surface hardness JIS K 6253, it measured using the Aska rubber hardness total A type by a polymers meter company.

[0053]** Based on tensile strength JIS K 6251, the sheet was pierced to the dumbbell-like No. 1 type, the tensile test was done on condition of for speed-of-testing/of 500 mm with the omnipotent tension tester, and tensile strength was measured.

[0054]** After pasting the above-mentioned thermally conductive resin sheet together to SUS304 board by 25-mm width and neglecting it for 20 minutes at 23 ** according to initial adhesion JIS Z 0237, it exfoliated on condition of for direction [of 180 **], and speed-of-testing/of 300 mm, peel strength was measured, and it was considered as initial adhesion.

[0055]

[Table 1]

| | 実施例 1 | 実施例 2 | 比較例 1 |
|------------------|------------|-------|-------|
| 樹脂組成物 (重量部) | 樹脂 | 100 | 100 |
| | 熱伝導性充填材 | 150 | 200 |
| | 発泡剤 | 2 | 2 |
| | シリコーンゴム | — | — |
| | シリコーンゴム硬化剤 | — | 1 |
| 発泡倍率 (倍) | 1.5 | 1.5 | — |
| 熱伝導性充填材配合量 (体積%) | 26.7 | 31.2 | — |
| 熱伝導率 (W/mK) | 1.72 | 2.71 | 1.1 |
| 表面硬度 (デュロメータ A) | 8 | 14 | 37 |
| 引張強度 (MPa) | 1.41 | 1.30 | 1.19 |
| 初期粘着力 (gf/25mm) | 540 | 531 | 253 |

[0056]In the thermally conductive resin sheet of the comparative example 1, thermal conductivity was as low as 1.1 W/mK, surface hardness was as high as the 37 durometers A, and tensile strength was as low as 1.19MPa so that clearly from Table 1. Initial adhesion was also as low as 253 gf(s)/25 m.

[0057]On the other hand, in the thermally conductive resin sheet of Examples 1 and 2, it turns out that thermal conductivity shows high thermal conductivity highly therefore compared with

the comparative example 1, and surface hardness is low rich in pliability, and tensile strength is high, and initial adhesion is high.

[0058]

[Effect of the Invention]As mentioned above, including elasticity resin and a thermally conductive filler, since the thermally conductive resin sheet concerning this invention is foam with low expansion ratio, it not only shows high thermal conductivity, but it is excellent in pliability and shape flattery nature, is excellent in the adhesion over an application site, and it is excellent [thermally conductive resin sheet] in the mechanical strength. Therefore, in the thermally conductive resin sheet of this invention, reinforcing members, such as glass fiber and glass fabrics, are not needed. Therefore, it can manufacture easily and cost can be reduced.

[0059]When it is used for the heat dissipation use of heating elements, such as an electric electronic component, application can make heat radiate efficiently easily, since it excels in the adhesion over an application site.

[Translation done.]